PCT
WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : B32B 27/30, G02B 1/04 | A1

(11) International Publication Number: WO 93/16878

(43) International Publication Date: 2 September 1993 (02.09.93)

(21) International Application Number: PCT/US92/10162

(22) International Filing Date: 25 November 1992 (25.11.92)

(30) Priority data:
07/842,275 25 February 1992 (25.02.92) US

(71) Applicant: THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US).

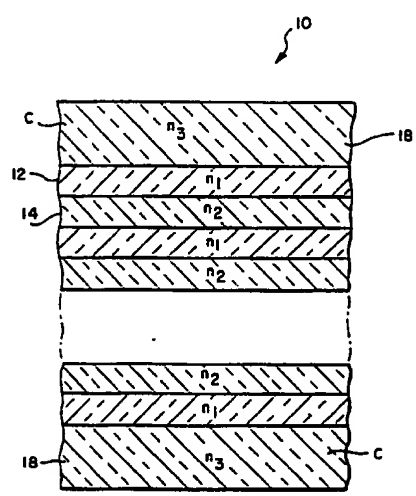
(72) Inventor: SCHRENK, Walter, J. ; 1307 Timber Drive, Midland, MI 48642 (US).

(74) Agent: HESSENAUR, Lloyd, E., Jr.; The Dow Chemical Company, Patent Department, P.O. Box 1967, Midland, MI 48641-1967 (US).

(81) Designated States: AU, CA, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: ALL-POLYMERIC ULTRAVIOLET REFLECTING FILM



(57) Abstract

An all-polymeric ultraviolet light reflective film which is lower in cost than previously used reflector materials, is weather resistant, and which does not absorb significant amounts of solar ultraviolet energy is provided. The film includes a sufficient number of alternating layers of at least first and second diverse polymeric materials which have an average percent transmission of greater than about 50 percent between wavelengths of 300 to 400 nm. A substantial majority of the individual layers of the film have optical thicknesses in the range where the sum of the optical thicknesses in a repeating unit of the polymeric materials is between 0.15 µm to 0.228 µm, and the first and second polymeric materials differ from each other in refractive index by at least about 0.03 in the wavelength range of from 300 to 400 nm. The reflective film is useful as a reflective material in solar detoxification systems, as a protective material in indoor and outdoor lighting systems, as a UV mirror in the fields of medical imaging, astronomical telescopes, and microscopy or in chemical reactions using UV radiation.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NL	Netherlands
BE	Belgium	GN	Guinea	NO	Norway
BF	Burkina Faso	GR	Greece	NZ	New Zealand
BG	Bulgaria	HU	Hungary	PL	Poland
BJ	Benin	IE	Ireland	PT	Portugal
BR	Brazil	IT	Italy	RO	Romania
CA	Canada	JP	Japan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo			SE	Sweden
CH	Switzerland	KR	Republic of Korea	SK	Slovak Republic
CI	Côte d'Ivoire	KZ	Kazakhstan	SN	Senegal
CM	Cameroon	LI	Liechtenstein	SU	Soviet Union
CS	Czechoslovakia	LK	Sri Lanka	TD	Chad
CZ	Czech Republic	LU	Luxembourg	TG	Togo
DE	Germany	MC	Monaco	UA	Ukraine
DK	Denmark	MG	Madagascar	US	United States of America
ES	Spain	ML	Mali	VN	Viet Nam
FI	Finland	MN	Mongolia		

ALL-POLYMERIC ULTRAVIOLET REFLECTING FILM

This invention relates to an all-polymeric ultraviolet reflecting film, and more particularly to a reflector which is substantially transparent to visible and near infrared wavelengths while reflecting a substantial portion of solar ultraviolet wavelengths.

The present invention provides an all polymeric ultraviolet light reflective film which is lower in cost than previously used reflector materials, is weather-resistant, and does not absorb significant amounts of solar ultraviolet energy. While a preferred use for the film of the present invention is as a reflective material in solar detoxification systems, the film also is useful in other applications where ultraviolet light reflectivity, but visible light transparency is required.

The terms "reflective", "reflectivity", "reflection", and "reflectance" as used herein refer to total reflectance (that is, ratio of reflected wave energy to incident wave energy) of a sufficiently specular nature. The use of these terms is intended to encompass semi-specular or diffuse reflection as well. In general, reflectance measurement refers to reflectance of light rays into an emergent cone with a vertex angle of 15 degrees centered around the specular angle. By the term "diverse" is meant that the polymeric materials need not differ in any respect except in terms of refractive index. Thus, while adjacent layers may be chemically diverse, if such materials have the same refractive index, then for purposes of the present invention they are not "diverse".

A specific intensity of reflectance, when used herein, is the intensity of reflection which occurs at a wavelength where no substantial absorption occurs. For example, the films of the present invention are designed to reflect ultraviolet light having wavelengths in the range of from about 300-400 nm. Light of other wavelengths, such as in the visible range, pass through (that is, are transmitted by) the films. It is at these ultraviolet wavelengths to which the intensity of reflection is referring.

Fig. 1 is a schematic cross section of a two component multilayer ultraviolet reflecting film of the present invention, the film including protective skin layers on both exterior surfaces thereof;

Fig. 2 is a perspective and somewhat schematic representation of a solar detoxification reflector system; and

Fig. 3 is a graph of wavelength versus predicted reflectance for multilayer films fabricated in accordance with the present invention.

The present invention provides improved multilayer all-polymeric ultraviolet reflecting films with a number of desirable properties including substantial ultraviolet reflectivity over the wavelength range of 300 to 400 nm while not absorbing any substantial amounts of ultraviolet radiation, substantial transparency to visible and near infrared light, and the capability of being laminated to substrates to form a number of useful articles. The optical theory of multiple reflections from layers having differing refractive indices demonstrates the dependency of the effect on both individual layer thickness and refractive index of the material. See, Radford et al, "Reflectivity of Iridescent Coextruded Multilayered Plastic Films", Polymer Engineering and Science 13, 3, pg. 216 (1973). The primary or first order reflected wavelength for a two component multilayer film for normal incidence is given by the equation below.

$$\lambda_I = 2(n_1 d_1 + n_2 d_2)$$

where, λ_I is the wavelength of first order reflection in nanometers, and spans the range of 300-400 nm, n_1 and n_2 are the refractive indices of the two polymers, and d_1 and d_2 are the layer thicknesses of the two polymers, also in nanometers.

For a three or more component film, the above equation may be generalized to:

$$\lambda_I = 2 \sum_{i-1}^{m} n_i d_i$$

where λ_I, n, and d are as defined above and m is an integer greater than 1. Thus, for example, for a three component film having a polymer repeating unit of ABCB, the equation is:

$$\lambda_I = 2(n_A d_A + n_B d_B + n_C d_C + n_B d_B)$$

If $d_A = d_B = d_C$, then the sum of the optical thicknesses in a repeat unit varies within the range of from 0.15 µm to about 0.20 µm. Preferably, the optical thickness range for each individual layer in the ABCB repeating unit to span 300 to 400 nm is from 0.025 µm to 0.036 µm.

As can be seen, the first order reflected wavelength is proportional to the sum of the optical thicknesses of the two polymers (where optical thickness, $n_i d_i$, is the product of layer thickness times refractive index). In addition to first order reflections, higher order reflections occur at integer fractions of the first order. The relative intensity of these higher order reflections depends on the ratio of the optical thickness of the polymer components

To produce a film which reflects a broad bandwidth of wavelengths in the range of from about 300 to 400 nm, a layer thickness gradient may be introduced across the thickness of the film. Thus, in one embodiment of the invention, the layer thicknesses will increase

monotonically across the thickness of the film. By monotonically, it is meant that the layer thicknesses increase at a predetermined rate across the thickness of the film. See, Schrenk, U.S. Patent No. 3,687,589. As can be seen from the above equations, variations in individual layer thickness, d, have a direct effect on the optical properties of the film.

The layer optical thicknesses needed for reflecting in the 300 to 400 nm range described above have all been described for reflectance of light at normal incidence (that is, 0°) on the film. The reflected wavelength varies with the angle of incidence of the solar energy. As the angle of incidence varies from 0° (normal incidence) to 45°, the shift is about 55 nm.

To accommodate the wavelength shift and the probability that not all light will strike the ultraviolet reflecting film at normal incidence, the layer optical thicknesses in the film may be designed to accommodate this somewhat larger range of 300 nm to 455 nm. While the film would reflect some visible light at normal incidence, it would be better able to reflect ultraviolet light at a range of angles of incidence. The maximum optical thicknesses of the layers in this design would increase about 15 percent, so that the sum of optical thicknesses in a repeating unit are in the range of from 0.15 µm to 0.228 µm. Such a design would insure that substantially all ultraviolet light impinging upon the film was reflected, even if the light were incident at an angle other than normal to the film.

Fig. 1 schematically illustrates a two-component ultraviolet reflective film 10 having a repeating unit AB in accordance with the present invention. The film 10 includes alternating layers of first polymer 12 having a refractive index, n_1, and a second polymer 14 having a refractive index, n_2. Fig. 1 shows a preferred form of the invention where substantially all of the layers of the film have optical thicknesses where the sum of the optical thicknesses of the repeat unit varies between 0.15 µm to 0.20 µm. Preferably, each individual layer has an optical thickness of between 0.07 µm and 0.11 µm. Fig 1 also depicts skin layers of a polymer (C) 18 positioned on both major exterior surfaces of the reflective body to protect the other layers from scratches or weathering or to provide support for the other layers.

Preferably, the polymers chosen have a refractive index mismatch of at least 0.03 at the wavelengths 300 to 400 nm. Typically, refractive indices of materials, including polymers, are measured at a convenient wavelength in the visible range such as 589 nm sodium vapor. It is known that refractive indices of polymers can increase at shorter wavelengths. However, it is difficult to measure refractive indices at ultraviolet wavelengths. We have found, however, that the refractive index mismatch of two diverse polymers, chosen based on published refractive indices at visible wavelengths, remains at least as large at ultraviolet wavelengths. Accordingly, choosing a refractive index mismatch of at least 0.03 will be a conservative estimate of the actual mismatch which occurs at ultraviolet wavelengths.

Preferably, for a three or more component system, the polymeric material having the highest refractive index differs from the polymeric material with the lowest refractive index

by at least about 0.03. The refractive indices of other components may be intermediate that of the components having the highest and lowest refractive index.

The polymeric materials utilized in the practice of the present invention are unique in the combination of properties that they must possess. The polymeric materials do not absorb any substantial amounts of ultraviolet radiation and inherently resist degradation by ultraviolet light without the addition of ultraviolet light absorbers. By this it is meant that the polymeric materials used in the practice of the present invention maintain an average percent transmission of greater than about 50 percent between 300 to 400 nm. As solar ultraviolet makes up only 3 to 4 percent of the total energy from the sun, absorption of significant amounts of the ultraviolet portion of the spectrum by a polymer severely detracts from its ability to find use in the present invention.

Generally, the individual polymers must be also substantially transparent to visible light, and preferably are also substantially transparent to wavelengths in the near infrared spectrum. As discussed above, the polymers must be resistant to degradation by ultraviolet light. Many thermoplastic polymers such as polystyrene and polyvinyl chloride are not resistant to degradation by ultraviolet radiation and must have incorporated therein UV absorbing compounds to improve stability. However, UV absorbing stabilizers will not function in the context of the present invention where non-absorption of ultraviolet radiation is a requirement.

Polymeric materials useful in the present invention include polymethyl methacrylate such as Cyro H15-012 (trademark) available from Cyro Industries (refractive index = 1.49), polyvinylidene fluoride such as Kynar (trademark) available from Atochem North America, Inc. (refractive index = 1.42), polychlorotrifluoroethylene such as Aclar 22A (trademark) available from Allied Signal Corporation (refractive index = 1.41), and polymethylpentene-1 such as TPX (trademark) available from Mitsui Chemicals (refractive index = 1.46). A preferred multilayer ultraviolet reflective film includes polyvinylidene fluoride as the first polymeric material and polymethyl methacrylate as the second polymeric material. Both polyvinylidene fluoride and polymethyl methacrylate have excellent stability and resistance to degradation in ultraviolet light as well as being nonabsorbers of ultraviolet light. In a preferred form, the reflective film includes relatively thick protective skin layers of polyvinylidene fluoride on each exterior surface and optically active alternating layers of polyvinylidene fluoride and polymethyl methacrylate in the interior.

It is preferred that the polymers selected have compatible rheologies for coextrusion. That is, as a preferred method of forming the multilayer films is the use of coextrusion techniques, the melt viscosities of the polymers must be reasonably matched to prevent layer instability or nonuniformity. The polymers used also should have sufficient interfacial adhesion so that the films will not delaminate. Alternatively, a third polymer may be used as an adhesive or glue layer to secure the first and second polymer layers together.

The multilayer ultraviolet reflective films of the present invention possess major advantages over prior art processes which use expensive metal and dielectric or chemical vapor deposition techniques. The films of the present invention can be tailored to reflect ultraviolet light over the 300 to 400 nm bandwidth; they can be readily coextruded and can have large surface areas; and they can be laminated to substrates which are shaped in a variety of useful articles such as a parabolic reflector.

Multilayer films in accordance with the present invention are most advantageously prepared by employing a multilayered coextrusion device as described in U.S Patent Nos. 3,773,882 and 3,884,606 the disclosures of which are incorporated herein by reference. Such a device provides a method for preparing multilayered, simultaneously extruded thermoplastic materials, each of which are of a substantially uniform layer thickness. Preferably, a series of layer multiplying means as are described in U.S. Patent No. 3,759,647 the disclosure of which is incorporated herein by reference may be employed.

The feedblock of the coextrusion device receives streams of the diverse thermoplastic polymeric materials from a source such as a heat plastifying extruder. The streams of resinous materials are passed to a mechanical manipulating section within the feedblock. This section serves to rearrange the original streams into a multilayered stream having the number of layers desired in the final film. Optionally, this multilayered stream may be subsequently passed through a series of layer multiplying means in order to further increase the number of layers in the final film.

The multilayered stream is then passed into an extrusion die which is so constructed and arranged that streamlined flow is maintained therein. Such an extrusion device is described in U.S. Patent No. 3,557,265, the disclosure of which is incorporated by reference herein. The resultant product is extruded to form a multilayered film in which each layer is generally parallel to the major surface of adjacent layers.

The configuration of the extrusion die can vary and can be such as to reduce the thickness and dimensions of each of the layers. The precise degree of reduction in thickness of the layers delivered from the mechanical orienting section, the configuration of the die, and the amount of mechanical working of the film after extrusion are all factors which affect the thickness of the individual layers in the final film.

The ultraviolet reflective films of the present invention find a number of uses As a primary example, they may be used as reflectors in a solar detoxification system. Such a system 20 is depicted schematically in Fig. 2. As shown, groundwater containing organic contaminants is pumped through line 22 by pump 24 to a series of solar reflector arrays 26 While only two such arrays are shown for simplicity, it will be understood that multiple arrays may be arranged in series or parallel to treat large quantities of contaminated water.

The reflector arrays 26 include parabolic-shaped solar ultraviolet reflecting film 28 laminated to a transparent substrate which reflects the ultraviolet portion of the sun's

energy back toward transparent tubing 30 through which the contaminated liquid flows. As previously explained, a catalyst, such as titanium dioxide, may either be mixed with the flowing liquid stream or mounted on a porous matrix within the tubing 30. The remainder of the solar energy (that is, wavelengths between 400 to 2100 nm) passes through reflecting film 28, including preferably both the visible and near infrared portions of the spectrum. This prevents undue heating of the liquid stream which would otherwise occur if all of the solar energy was concentrated on the tubing. Alternatively, the visible and infrared solar energy transmitted through the reflector arrays may be collected or concentrated separately for other processes requiring solar heating.

However, in some instances, it may be desirable to provide some heating to the liquid to enhance a particular catalyzed degradation reaction. In those instances, the reflecting film of the present invention may be designed to reflect some or all of the solar visible and/or infrared energy. This may be accomplished by laminating the all polymeric ultraviolet reflective film of the present invention to a broadband visible and near infrared (400 to 2100 nm) all polymeric reflecting film.

Alternatively, a sufficient number of layers having optical thicknesses in the range needed to reflect the desired amount of visible and/or infrared energy may be coextruded with the ultraviolet reflecting layers. As taught in the above-referenced applications, such layers may be optically thick (>0.45 µm) or a combination of optically thick and optically very thin (<0.09 µm), with a portion of the layers being optically thin (<0.09 µm and <0.45 µm), where optical thickness is defined as the product of actual layer thickness and refractive index of the polymer making up the layer.

After catalytic treatment and exposure to the solar ultraviolet energy, the treated liquid may be sent, for example, to a holding basin 33. From there, it may be pumped, via pump 32 and line 34, either back underground or to a commercial or industrial plant for use.

Other uses of the ultraviolet reflecting film of the present invention include UV mirrors which are used in the fields of medical imaging, astronomical telescopes, and microscopy. Chemical reactions also use ultraviolet light as a curing mechanism. The reflecting film of the present invention may be used to reflect or concentrate such radiation onto chemical reactants. Ultraviolet radiation is also used as a tool for sterilization. The UV reflective films of the present invention may find use in directing ultraviolet radiation onto articles to be sterilized. Other outdoor uses for the films of the present invention include laminating the film to windows or skylights to protect interior furnishings from the degradative effects of ultraviolet light. For example, the ultraviolet reflecting films of the present invention could be laminated to or included in automotive window glass to protect the interior upholstery and dashboard.

There is also a need for ultraviolet reflective films in indoor lighting to protect persons, foods, clothing or furniture from the harmful, degradative effects of ultraviolet light.

The reflective films of the present invention could be fabricated into protective tubes around fluorescent light sources. As the film is transparent to visible light, no loss of visible light would occur. Rather, only the undesired ultraviolet radiation would be contained Ultraviolet light is known to be harmful to the human eye. The UV reflective film of the present invention may find use in sunglasses or welders' goggles. The film could be used in umbrellas to prevent ultraviolet radiation from reaching the skin of a person. Further, the film could be used to block UV light from reaching and causing fading and degradation to clothing and furniture Microlithography, industrial micro-machining, and ultraviolet laser reflection are other fields in which the ultraviolet reflecting films of the present invention may find use.

In order that the invention may be more readily understood, reference is made to the following examples, which are intended to be illustrative of the invention, but are not intended to be limiting in scope.

Example 1

To demonstrate the ultraviolet reflecting capabilities of the film of the present invention, a computer simulation was run to predict the reflectance characteristics of a two-component polymethyl methacrylate/polyvinylidene fluoride multilayer film. The simulation used a software program entitled "Macleod Thin Film Optics" available from Kidger Optics, Sussex, England. The sum of the optical thicknesses of the layers in the AB repeat unit of the film were assumed to be in the range of from 0.15 µm to 0.20 µm, and the individual layers were assumed to have optical thicknesses in the range of 0.07 µm to 0.11 µm. A refractive index mismatch of 0.07 was assumed based on the actual mismatch of the two polymers when measured at visible wavelengths.

Fig. 3 depicts the predicted reflectance results for films having 100, 200, 400, 650, and 1300 alternating layers, respectively. As can be seen, as the number of layers in the multilayer film increases, the predicted reflectance of the film approaches 100 percent reflectance in the wavelength range of 300 to 400 nm. This demonstrates the strong ultraviolet light reflecting capabilities of the multilayer films of the present invention.

1. An ultraviolet light reflective all-polymeric film of at least first and second diverse polymeric materials which do not absorb significant amounts of ultraviolet radiation, the film comprising a sufficient number of alternating layers of said first and second polymeric materials such that at least 30 percent of ultraviolet light of a wavelength of between 300 to 400 nm incident on said film is reflected, said first and second polymeric materials having an average percent transmission of greater than 50 percent between wavelengths of 300 to 400 nm, a substantial majority of the individual layers of said film having optical thicknesses in the range where the sum of the optical thicknesses in a repeating unit of said polymeric materials is between 0.15 µm to 0.228 µm, and wherein said first and second polymeric materials differ from each other in refractive index by at least about 0.03 in the wavelength range of from 300 to 400 nm.

2. The ultraviolet light reflective polymeric film of claim 1 in which said individual layers have optical thicknesses of between 0.07µ m to 0.11 µm.

3. The ultraviolet light reflective polymeric film of claim 1 in which said first polymeric material is polyvinylidene fluoride and said second polymeric material is polymethyl methacrylate.

4. The ultraviolet light reflective polymeric film of claim 1 in which said first polymeric and second polymeric materials are selected from the group consisting of polymethyl methacrylate, polyvinylidene fluoride, polychlorotrifluoroethylene, and polymethylpentene-1.

5. The ultraviolet light reflective polymeric film of claim 1 in which said film comprises at least 200 layers.

6. The ultraviolet light reflective polymeric film of claim 1 in which at least 80 percent of ultraviolet light of a wavelength of between 300 to 400 nm incident on said film is reflected.

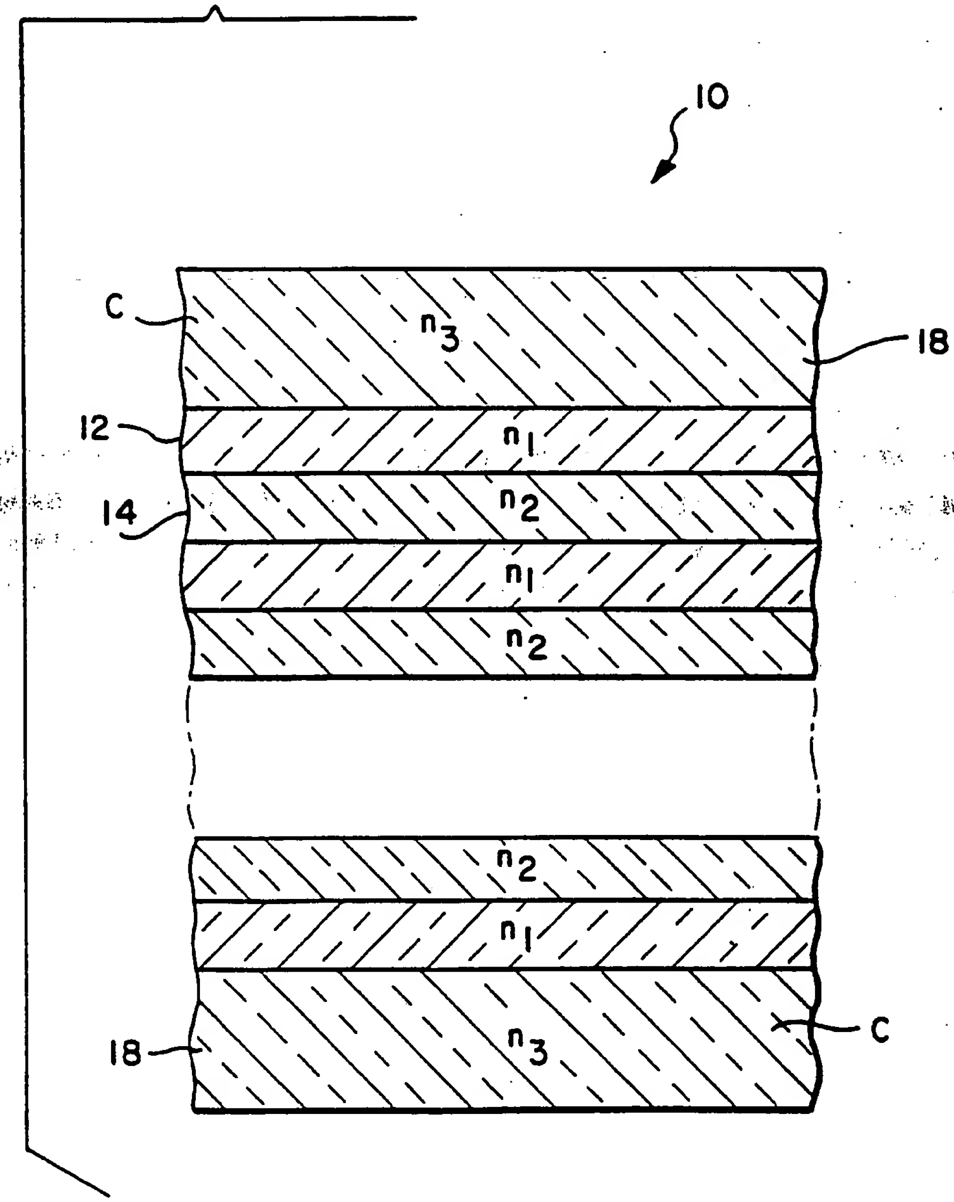
7. The ultraviolet light reflective polymeric film of claim 1 in which said polymeric film includes first, second, and third diverse polymeric materials of alternating layers in a repeating unit ABCB.

8. The ultraviolet light reflective polymeric film of claim 1 in which said polymeric film includes first, second, and third diverse polymeric materials of alternating layers in a repeating unit ABC.

9. The ultraviolet light reflective polymeric film of claim 1 in which said polymeric film has been laminated or coextruded with a transparent substrate material or with a visible and/or infrared light reflecting body.

10. The ultraviolet light reflective polymeric film of claim 1 in which the film includes protective skin layers on either or both major exterior surfaces of said film.

FIG-1



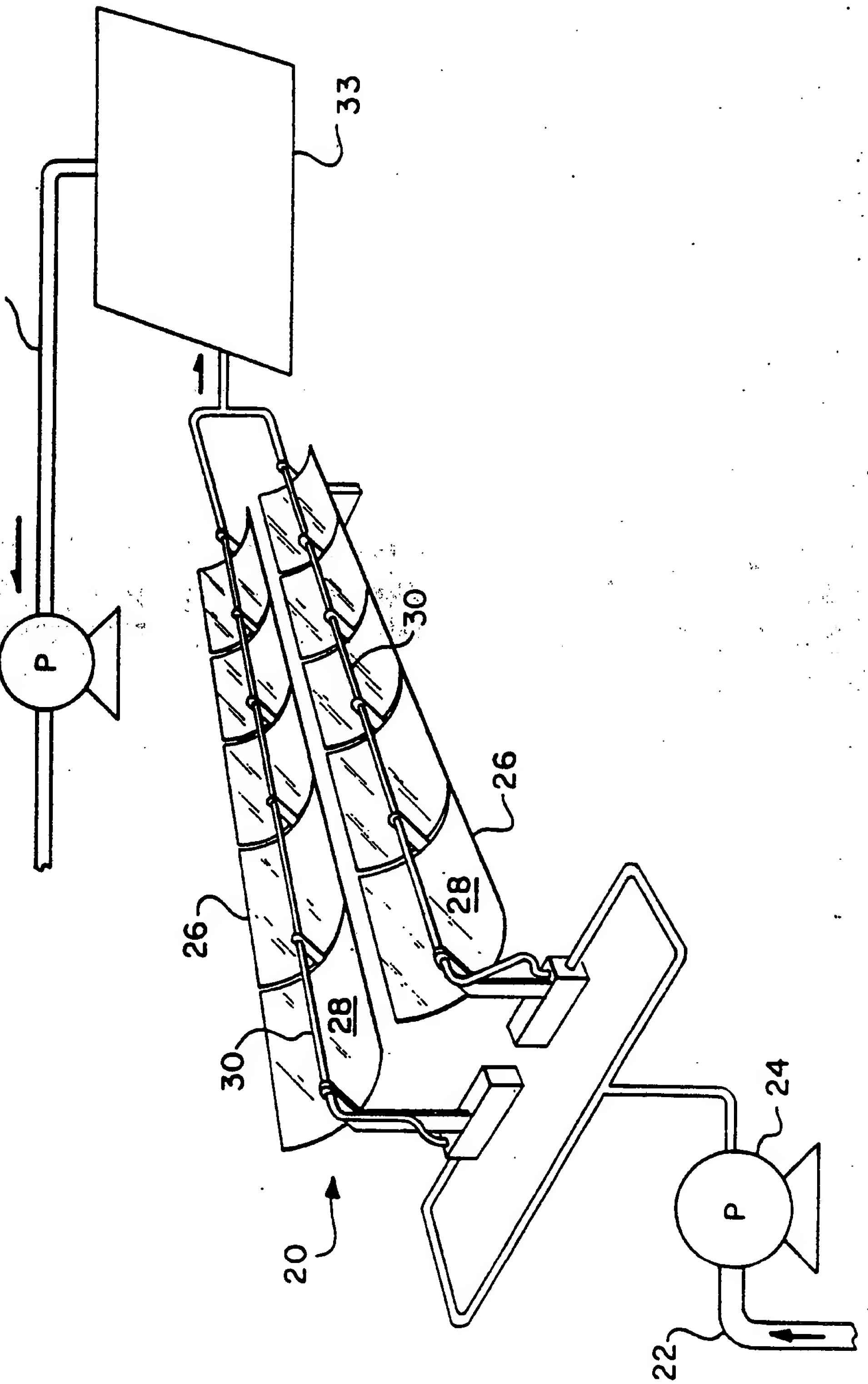


FIG-2

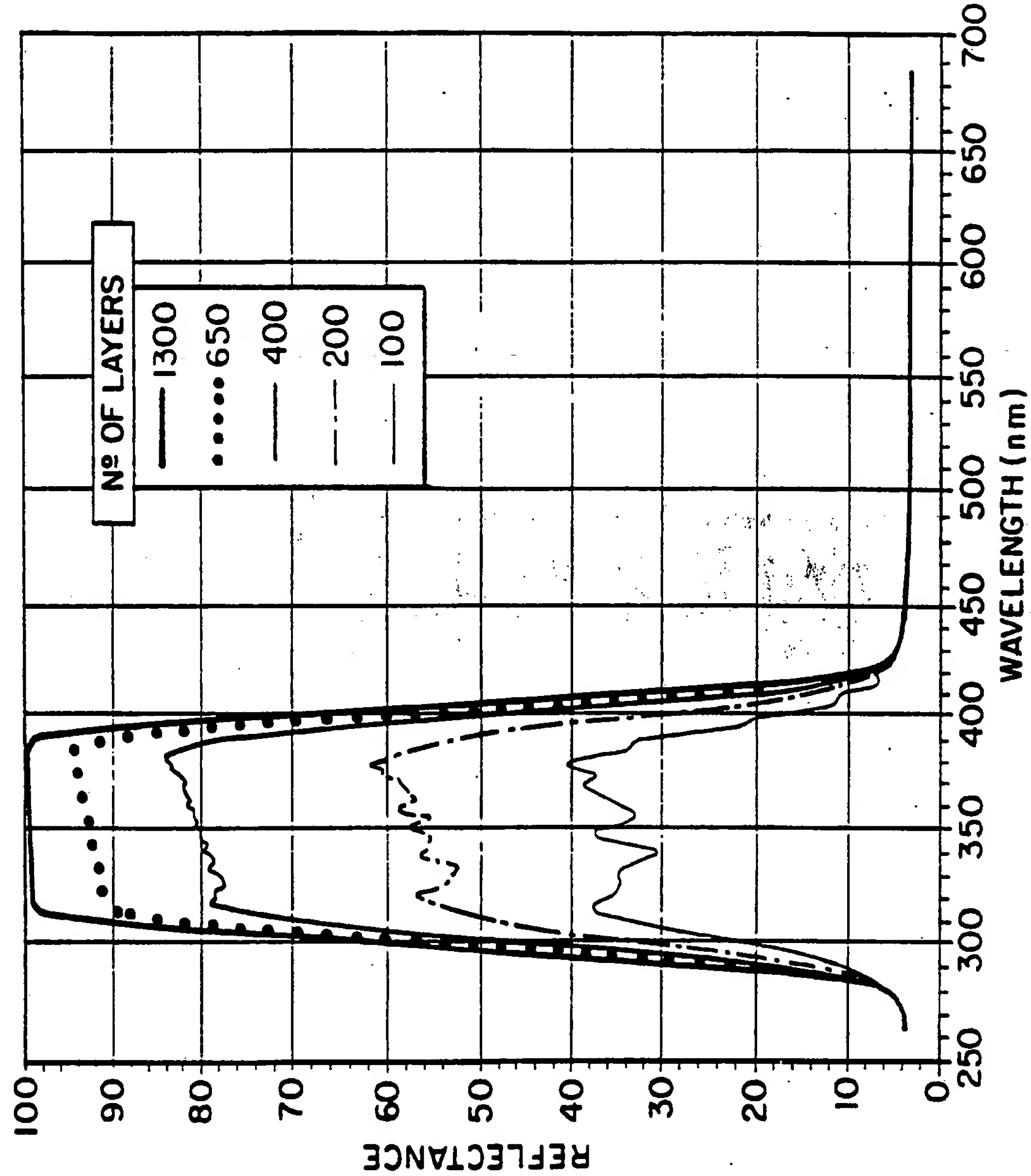

Nº OF LAYERS
1300
650
400
200
100
REFLECTANCE
100
90
80
70
60
50
40
30
20
10
0
250
300
350
400
450
500
550
600
650
700
WAVELENGTH (nm)

FIG-3

INTERNATIONAL SEARCH REPORT

.ternational application No.
PCT/US 92/10162

A. CLASSIFICATION OF SUBJECT MATTER

IPC5: B32B 27/30, G02B 1/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC5: B32B, G02B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP, A2, 0404463 (THE DOW CHEMICAL COMPANY), 27 December 1990 (27.12.90), abstract; page 5, line 14-21; page 7, line 3-4 and 7; example 3	1-10
	--	
X	EP, A2, 0469732 (THE DOW CHEMICAL COMPANY), 5 February 1992 (05.02.92), abstract; column 7, line 10 and 45-47; column 2, line 53-54; column 11, line 23,26-27 and 40-42; column 10, line 29-31	1-10
	--	
X	US, A, 3711176 (ALFREY, JR. ET AL), 16 January 1973 (16.01.73), abstract; column 5, line 15-20; column 6, line 63-68	1-10
	--	

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" erlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priori: date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combinatic being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 March 1993	01.04.93
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer ANITA SKEPPSTEDT

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, E, 31780 (COOPER ET AL), 25 December 1984 (25.12.84), abstract; column 1, line 25-29 and 32-35; table 1	1-10

--

SA ' ' 716

INTERNATIONAL SEARCH REPORT

Information on patent family members

29/01/93

International application No.
PCT/US 92/10162

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A2- 0404463	27/12/90	AU-B- 622812	16/04/92
		AU-A- 5758790	03/01/91
		CA-A- 2019272	20/12/90
		CN-A- 1048191	02/01/91
		JP-A- 3041401	21/02/91
		US-A- 5122905	16/06/92
		US-A- 5122906	16/06/92
EP-A2- 0469732	05/02/92	JP-A- 4313704	05/11/92
		US-A- 5103337	07/04/92
US-A- 3711176	16/01/73	NONE	
US-A- 31780	25/12/84	NONE	